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The First Step in the Swelling of Gelatin with Water. IV

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By the aid of a simple model of the constitution of the interference plate it is possible to explain the peculiar phenomenon that the lower edge of the extinction band by aftertreatment in some cases takes up more silver bromide than the upper edge. The same model makes it possible to calculate the diameter of the gelatin molecule.

1. AFTERTREATMENT OF THE PLATE

In spite of the very detailed recipe which the late civil engineer Herman Christensen has given for the preparation of his interference gelatin plate [1], and in spite of the practice which I have afterwards developed during the preparation of some 250 plates, it still is a rather delicate job to prepare a really first class plate. Especially the colour is very often too weak.

To overcome this difficulty I have tried to give the finished plates an aftertreatment with silver nitrate and potassium bromide, exactly in the same way as during the original preparation, and it is in this way possible to arrive at much stronger colours and, by varying the concentration of the silver nitrate solution, to obtain any desired colour and, finally, through repetition of the procedure, nearly opaque plates.

By this procedure the concentration of silver bromide is of course increased and, by repeated aftertreatment, the percentage by volume can reach values higher than 60.

In order to get the greatest possible material the original plates (9 × 12 cm) were cut in small pieces (18 × 20 mm) which were indicated by small index figures, *e.g.* 47_3, and examined separately. In this way a total of 30 pieces of 6 different plates have been aftertreated, 13 of them two times and 5 three times, 57 measurements in all of both the upper and the lower edge of the broad band.

The silver nitrate solutions had the concentrations 25:100, 11:100 and 5:100. The first one was applied for 3 or 1 1/4 min with identical results, the second one for 3 min and the third one for 6 min. 24 pieces were treated with the strongest solution, 9 with the intermediate one and 6 with the most diluted solution. The results are shown in Tables 1, 2 and 3.

Table 1. First aftertreatment.

$AgNO_3$ 25:100, 3 min.

Plate No.	I		II	
	v_A	Δv_A	v_A	Δv_A
181_3	37.3	9.9	30.0	11.0
212_3	34.8	9.4	24.0	9.9
216_8	30.1	8.2	20.8	10.9
50_{11}	30.1	11.6	20.3	8.6
47_1	29.3	11.5	20.4	8.4
216_{12}	28.6	12.9	22.6	8.4
50_8	28.4	12.9	18.7	8.0
50_5	27.9	12.0	19.2	9.1
47_4	27.2	13.6	18.3	9.7
47_9	26.9	13.3	17.0	10.0
196_7	25.0	13.5	15.4	10.6
196_5	24.6	12.6	16.0	9.9
196_9	23.7	13.0	15.4	11.0

$AgNO_3$ 25:100, 1 1/4 min.

Plate No.	I		II	
	v_A	Δv_A	v_A	Δv_A
181_2	36.9	13.7	30.4	13.6
212_{10}	36.7	14.6	26.0	15.5
212_4	34.8	8.7	22.8	11.3
216_4	31.0	8.3	21.5	10.7
47_5	29.1	13.1	18.7	11.6
47_2	27.7	13.4	19.3	10.1
47_8	27.2	13.8	18.1	9.3
47_{10}	24.6	16.1	16.0	9.9
196_{10}	24.6	13.7	16.2	10.7
196_3	24.3	11.0	16.2	8.4
196_8	24.2	12.9	18.0	9.1

$AgNO_3$ 11:100, 3 min.

Plate No.	I		II	
	v_A	Δv_A	v_A	Δv_A
181_4	37.4	4.6	29.5	7.6
212_5	34.8	6.6	22.8	8.6
216_9	31.0	8.1	21.1	8.4
47_7	29.1	7.3	19.6	5.4
50_{14}	28.3	8.0	19.2	5.8
50_{18}	27.7	7.3	18.5	5.3
47_3	27.2	6.6	18.1	4.7
196_6	24.6	5.5	16.3	5.4
196_4	23.9	5.8	15.8	5.7

$AgNO_3$ 5:100, 6 min.

Plate No.	I		II	
	v_A	Δv_A	v_A	Δv_A
181_7	37.7	5.3	31.7	7.2
212_{11}	35.2	4.5	22.8	4.6
216_{10}	30.8	4.5	21.5	5.2
50_4	28.9	5.0	17.8	4.2
47_6	26.5	4.8	16.9	3.7
196_{11}	22.7	3.5	15.6	4.7

The figures I and II refer to the upper and the lower edge of the broad band. The first column gives the number of the plate, the second the value of v_A, the percentage by volume of silver bromide, and the third the increase in v_A by the aftertreatment.

2. RESULTS OF THE AFTERTREATMENT

With exception of the plates, which have in advance been watered, the increase in v_A is, for each concentration of silver nitrate, independent of the original value of v_A.

Table 2. Second aftertreatment.

$AgNO_3$ 25:100, 3 min.

	I		II	
Plate No.	v_A	Δv_A	v_A	Δv_A
47_1	40.8	4.7	28.8	5.7
216_{12}	41.5	7.6	31.0	11.0
47_4	40.8	6.0	28.0	2.1
47_9	40.2	7.3	27.0	2.1
196_5	37.2	8.8	25.9	7.5
196_9	36.7	7.1	26.4	8.2

$AgNO_3$ 25:100, 1 1/4 min.

	I		II	
Plate No.	v_A	Δv_A	v_A	Δv_A
212_{10}	51.3	11.0	41.5	11.0
47_5	42.2	9.2	30.3	9.2
47_2	41.1	4.5	29.4	3.8
47_8	41.0	4.9	27.4	4.2
47_{10}	40.7	12.3	25.9	8.6
196_{10}	38.3	6.7	26.9	7.5
196_8	37.1	10.7	27.1	8.4

$AgNO_3$ 11:100, 3 min.

	I		II	
Plate No.	v_A	Δv_A	v_A	Δv_A
212_5	41.4	3.0	31.4	5.7
216_9	39.1	7.0	29.5	3.0
47_3	33.8	9.4	22.8	4.6

$AgNO_3$ 5:100, 6 min.

	I		II	
Plate No.	v_A	Δv_A	v_A	Δv_A
212_{11}	40.3	1.9	27.4	2.6
47_6	31.3	0.7	20.6	0.7
196_{11}	26.2	2.6	20.3	0.9

In most cases the increases in v_A are higher for the upper than for the lower edge of the broad band, as could be expected. This is the case for the No. 47 (10 cases), 50 (6 cases), 196 (8 cases and 1 exception), whereas No. 181 (4 cases), 212 (4 cases and 1 exception) and 216 (5 cases) show the opposite phenomenon.

As explained earlier [2] the broad band originates from a series of layers whose percentages by volume of silver bromide are so great and lie

Table 3. Third aftertreatment.

$AgNO_3$ 11:100, 3 min.

	I		II	
Plate No.	v_A	Δv_A	v_A	Δv_A
216_9	46.1	2.8	32.5	6.8
47_3	43.2	6.7	27.4	4.3

$AgNO_3$ 5:100, 6 min.

	I		II	
Plate No.	v_A	Δv_A	v_A	Δv_A
212_{11}	42.2	2.7	30.0	4.8
196_{11}	28.8	2.6	21.2	4.8

so near each other, that the individual interference bands merge into one broad band. These layers go from the air side of the coating and into about 2/3 of the whole thickness of the coating. In the next following part of the coating the concentration of silver bromide decreases rapidly so that the individual bands are separated from each other and thereby constitute the so-called fringes.

It appears from this, that v_A is always lower at the lower than at the upper end of the broad band. The most probable explanation why the increase of v_A in a number of cases nevertheless is higher at the lower edge than at the upper edge seems to be that the silver bromide is dispersed in the form of grains, and that these grains at the lower edge are so much smaller than those at the upper edge that the larger surface of these smaller grains more than compensates for the lower concentration.

However, the further development of this explanation leads to great difficulties, especially in respect of the understanding of the different steps of the swelling process [3]. On the other hand, it is possible on the basis of a simple model of the constitution of the plate to give an entirely different explanation of these peculiarities.

3. THE CONSTITUTION OF THE PLATE

In a previous paper [4] I have assumed that the polar groups of the gelatin molecule are found on one side of the molecule, which is therefore hydrophilic, whereas the non-polar groups are found on the other side, which is therefore hydrophobic. The silver bromide is situated between two adjacent hydrophilic surfaces, and the corresponding percentage by volume, G′, of unhardened gelatin is therefore divided in two halves.

4. THE COURSE OF THE AFTERTREATMENT

By aftertreatment with silver nitrate, which is terminated already after 1 1/4 min, the solution must at once fill the space v_0 between the adjacent hydrophobic surfaces but has no time for diluting the solutions of soluble gelatin [5], which are distributed throughout the network of gelatin molecules. On the other hand, the silver ions have the possibility of being adsorbed on the already present surfaces of silver bromide.

By the subsequent treatment with potassium bromide (20:100), the silver nitrate, which fills the space v_0, must immediately be converted into silver bromide, and the same is the case with some of the adsorbed silver ions on the surface of the silver bromide.

During the following treatment (6 min) with the mixed solution of potassium bromide and potassium metabisulphite the rest of the adsorbed silver ions are converted into silver bromide, and the molecular silver bromide in the volume v_0 is dissolved by the metabisulphite and then transported to and adsorbed on the surface of the layer of silver bromide, which thereby thickens.

Table 4.

$AgNO_3$ 25:100							
Plate No.	number of pieces	I				II	
		Δv_A mean	v_0 mean	ΔS	ΔA	Δv_A mean	ΔA
47	7	13.2	61	2.6	10.6	9.7	7.1
196	6	12.8	90	3.8	9.0	9.8	6.0
212	2	9.0	107	4.5	4.5	10.8	6.3
216	2	8.2	75	3.2	5.0	10.8	7.6

Table 5.

$AgNO_3$ 11:100						
Plate No.	number of pieces	I			II	
		Δv_A mean	ΔS	ΔA	Δv_A mean	ΔA
47	2	7.4	1.3	6.1	5.4	4.3
196	2	5.6	1.9	4.7	5.6	3.7
212	1	6.6	2.2	4.4	8.6	6.4
216	1	8.1	1.6	6.5	8.4	6.8

Table 6.

$AgNO_3$ 5:100						
Plate No.	number of pieces	I			II	
		Δv_A	ΔS	ΔA	Δv_A	ΔA
47	1	4.8	0.5	4.3	3.7	3.2
196	1	3.5	0.8	2.7	4.7	3.9
212	1	5.1	0.9	4.2	4.6	3.7
216	1	4.5	0.7	3.8	5.2	4.5

The increase in v_A through the aftertreatment is therefore made up of two parts, the directly adsorbed quantity ΔA, and the quantity ΔS subsequently transported from v_0.

1. For the silver nitrate solution 25:100 one volume corresponds to the following volume of silver bromide:

$$\frac{25 \times 1.194 \times 1.14}{125 \times 6.46} = 0.0422$$

where 1.194 is the density of the solution, 1.14 the previously[6] found value of the quotient AgBr:AgNO$_3$, and 6.46 the density of silver bromide.

For the solutions 11:100 and 5:100 the figures are 0.0209 and 0.0088, respectively.

2. For the four plates whose values of v_0 are experimentally determined[7] the data are collected in Tables 4, 5 and 6.

For the second and third aftertreatment there are fewer observations, and the results therefore are not very exact. See Tables 7 to 11.

Table 7. Second aftertreatment.

AgNO$_3$ 25:100					
		I		II	
Plate No.	number of pieces	Δv_A mean	ΔA	Δv_A mean	ΔA
47	6	6.6	4.0	5.1	2.5
196	4	8.2	4.4	7.9	4.1
212	1	—	—	11.0	6.5
216	1	7.6	4.4	11.0	7.8

Table 8.

AgNO$_3$ 11:100					
		I		II	
Plate No.	number of pieces	Δv_A	ΔA	Δv_A	ΔA
47	1	7.0	5.7	4.6	3.3
212	1	3.0	0.8	5.7	3.5
216	1	7.0	5.4	3.0	1.4

Table 9.

AgNO$_3$ 5:100					
		I		II	
Plate No.	number of pieces	Δv_A	ΔA	Δv_A	ΔA
47	1	0.7	0.2	0.7	0.2
196	1	2.6	1.8	0.9	0.1
212	1	1.9	1.0	2.6	1.7

Table 10. Third aftertreatment.

AgNO$_3$ 11:100					
		I		II	
Plate No.	number of pieces	Δv_A	ΔA	Δv_A	ΔA
47	1	6.7	5.4	4.3	3.0
216	1	2.8	1.2	6.8	5.2

Table 11.

AgNO$_3$ 5:100					
		I		II	
Plate No.	number of pieces	Δv_A	ΔA	Δv_A	ΔA
196	1	2.6	1.8	4.8	4.0
212	1	2.7	1.8	3.1	2.2

The adsorbed amount of silver bromide ΔA is supposed to form a compact layer the thickness of which can be either the total length of a molecule of silver bromide or — on the average — half this value, if the layer consists of only single silver or bromide ions. The total length of the silver bromide molecule is known to be 0.64 mμ, and it is consequently to be expected that the thickness of the layer is either 0.32 or 0.64 mμ.

If the value of G′, the percentage by volume of unhardened gelatin, is known it must therefore be possible to calculate the diameter of the gelatin molecule because

$$\frac{G'}{2d_G} = \frac{\Delta A}{0.64} \quad \text{or} \quad \frac{G'}{d_G} = \frac{\Delta A}{0.32}$$

where d_G is the diameter of the gelatin molecule. It is multiplied by 2 because the silver bromide is situated between two surfaces of unhardened gelatin, and therefore corresponds to two diameters of gelatin molecules.

From earlier measurements [8] it is known that the values of G′ for the upper edge of the broad band vary from 30.2 to 34.2, with the mean value 31.4, for the lower edge from 21.9 to 22.2 mean 22.2. I assume that these values also are valid for the new measurements. By inserting these values in the equation above we find for the first aftertreatment with the strongest solution of silver nitrate the following values of d_G. (See Table 12).

Table 12.

	I		II		
Plate No.	d_{AgBr}	d_G	d_{AgBr}	d_G	d_G mean
47	0.64	0.93	0.64	0.91	0.92
196	0.64	1.12	0.64	1.18	1.15
212	0.32	1.11	0.64	1.13	1.12
216	0.32	1.00	0.64	0.94	0.97

The table shows that no intermediary values are possible between 0.32 and 0.64, and this fact seems to be the real cause of the peculiar phenomenon that v_A for some plates (212,216) are greater for the lower edge than for the upper edge of the broad band.

The calculated values of d_G agree well with the values 0.8—0.9 mμ which Sheppard, Lambert and Swinehart [9] have assumed earlier.

For the more diluted solutions of silver nitrate and for the second and third aftertreatment the results are scant and not very exact. By using the now known values for d_G we find the corresponding values for the thickness of the silver bromide layer, which are collected in Tables 13 to 15.

Table 13.

AgNO$_3$ 25:100				
Plate No.	I		II	
	aftertr.		aftertr.	
	1	2	1	2
47	0.64	0.23	0.64	0.21
196	0.64	0.32	0.64	0.42
212	0.32	—	0.64	0.65
216	0.32	0.27	0.64	0.68

Table 14.

AgNO$_3$ 11:100						
Plate No.	I			II		
	aftertr.			aftertr.		
	1	2	3	1	2	3
47	0.36	0.33	0.32	0.36	0.27	0.25
196	0.34	—	—	0.38	—	—
212	0.31	0.06	—	0.64	0.35	—
216	0.40	0.33	0.07	0.60	0.12	0.45

Table 15.

AgNO$_3$ 5:100						
Plate No.	I			II		
	aftertr.			aftertr.		
	1	2	3	1	2	3
47	0.25	0.01	—	0.27	0.02	—
196	0.20	0.13	0.13	0.40	0.00	0.42
212	0.30	0.07	0.13	0.37	0.17	0.22
216	0.24	—	—	0.39	—	—

The figures I and II refer to the upper and the lower edge of the broad band. Column 1 shows the number of the plate, and the following columns the calculated thicknesses of the silver bromide layer for the first, the second and the third aftertreatment, if any.

For the first aftertreatment the values 0.32 and 0.64 seem to be valid for all concentrations of silver nitrate. It is worth noting that also for the concentration 11:100 the lower edge takes up more silver bromide than the upper edge, in the same two cases as before.

The measurements of the following aftertreatments are too scant and uncertain to permit any conclusions.

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